5. Synthesis and Dimerization of Bicyclo[4.4.1]undec-1(11)-ene, a Bridged *trans*-Cycloheptene[1])

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Summary

The synthesis of bicyclo[4.4.1]undec-1(11)-ene (**5**) by intramolecular *Wittig* reaction is described. The *Bredt* olefin could not be isolated, but dimerized rapidly to a novel compound **15** containing a cyclopropane ring. The olefin **5** was trapped *in situ* by 2,5-diphenylbenzo[*c*]furan.

Introduction. - The question of the limits of *Bredt*'s rule is of considerable current interest [1] [2]. It is now generally accepted that the strain of a bicyclic or polycyclic bridgehead olefin (*Bredt* olefin) is comparable to the strain of the corresponding *trans*-cycloalkene from which it may be formally derived by bridging. This hypothesis, advocated by *Wiseman* in 1967 [3], has been supported by experimental evidence from a large number of synthetic approaches to different *Bredt* olefins and by two independent force-field calculations [4] [5].

However, within a series of homologous bridged *trans*-cyclooctenes, *trans*-cycloheptenes, and *trans*-cyclohexenes, the principles which govern relative strain energies are not obvious. *Köbrich* [1] formulated a rule ('rule A'), according to which increasing the number of carbon atoms in the bridge should decrease the strain of the *Bredt* olefins. Indeed, whereas the ethylene-bridged *trans*-cycloheptenes bicyclo[3.2.2]non-1-ene (**1**) and bicyclo[3.2.2]non-1(7)-ene (**2**) could be generated in 65% combined yield by pyrolysis of the corresponding bridgehead trimethylammonium hydroxide and observed by low temperature NMR. [6], the same method gave less than 1% yield of the methylene-bridged *trans*-cycloheptenes, bicyclo[3.2.1]oct-1-ene (**3**) and bicyclo[3.2.1]oct-1(7)-ene (**4**) [7]. However, according to force-field calculations [4], relative strain energies of bridged *trans*-cycloheptenes do not follow a regular pattern, but are the result of subtle conformational differences not related to the total number of carbon atoms.

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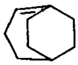
[1]) Taken in part from the planned dissertation of *J.C.* Presented at the meeting of the Swiss Chemical Society, 20.10.1978.

To solve this question, the synthesis of bicyclo[4.4.1]undec-1(11)-ene (**5**), a tetramethylene-bridged *trans*-cycloheptene, was undertaken. According to *Köbrich*'s rule A, *Bredt* olefin **5** should be the least strained *trans*-cycloheptene. Its unique structure also eliminates the formal ambiguity of geometrical double-bond isomers [8], because *cis-trans* isomerization leads to the mirror image, *i.e.* remains without effect in the racemic compound.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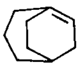
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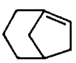
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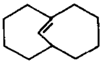
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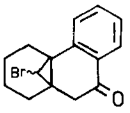
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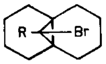
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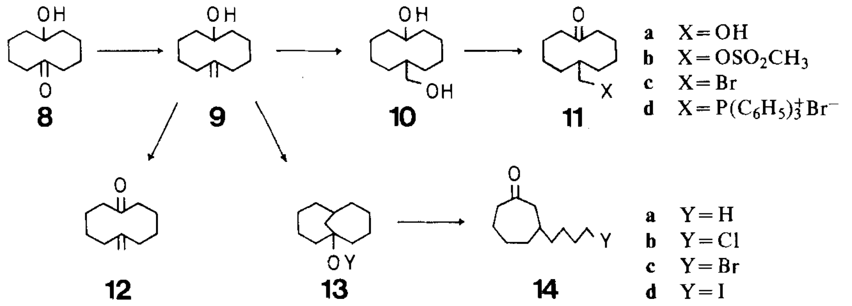
The reaction of *syn*- and *anti*-11-bromo-4,5-benzotricyclo[4.4.1.$0^{1,6}$]undec-4-en-3-one (**6**) with tetraethylammonium acetate in acetone yields the corresponding acetate by substitution with retention. There is good evidence that the reaction proceeds by HBr elimination to the *cis-trans* isomeric bridgehead trienones containing the bicyclo[4.4.1]undec-1(11)-ene unit, followed by addition of acetic acid [9]. Substituted bicyclo[4.4.1]undec-1(11)-enes were also postulated as intermediates in the silver ion catalyzed solvolyses of various 11-bromotricyclo-[4.4.1.$0^{1,6}$]undecane derivatives **7** [10]. It is therefore of interest to know, whether the parent *Bredt* olefin **5** can be generated and isolated under non-solvolytic conditions.

The intramolecular *Wittig* reaction is the method of choice for the synthesis and isolation of methylene-bridged *trans*-cyclooctenes [11], and also proved effective for the generation of the unstable bicyclo[3.2.1]oct-1(7)-ene (**4**) [12]. It was therefore applied to the preparation of bicyclo[4.4.1]undec-1(11)-ene (**5**).

Syntheses. - The reaction of 6-hydroxycyclodecanone (**8**) [13] with methylenetriphenylphosphorane in dimethylsulfoxide led to 6-methylenecyclodecanol (**9**) [14] *(Scheme 1)*. Hydroboration and oxidation gave 6-(hydroxymethyl)cyclodecanol (**10**). Selective oxidation of the secondary in the presence of the primary HO-group was accomplished with bromine and hexamethylphosphoric triamide in methylene chloride [15] in almost quantitative yield. 6-(Hydroxymethyl)cyclodecanone (**11a**) was transformed into the required triphenylphosphonium bromide **11d** by sequential treatment with methanesulfonyl chloride and triethylamine in methylene chloride, lithium bromide in refluxing acetone, and triphenylphosphine in a minimum of dry ether at 130°.

Scheme 1

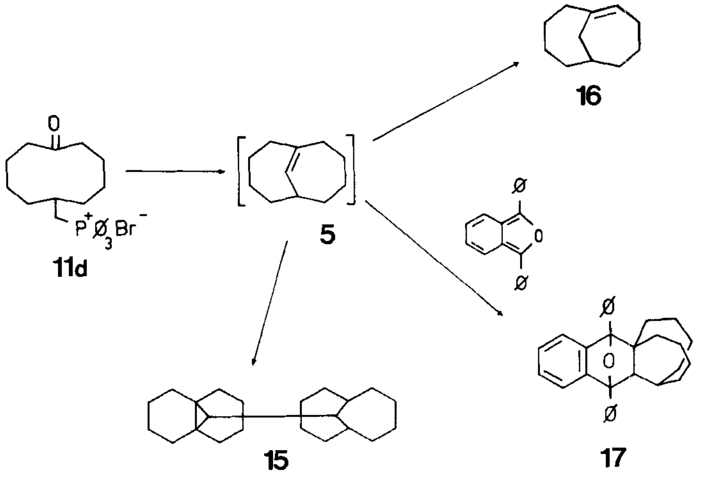


Other routes to 6-(halomethyl)cyclodecanones were explored. Oxidation of 6-methylenecyclodecanol (**9**) with chromic trioxide in pyridine [16] gave 6-methylenecyclodecanone (**12**). However, the light-induced radical-chain addition of HBr to **12** in pentane solution [17] did not yield any bromide **11c**. Also fruitless were several attempts to protect the keto function in **12** owing to the high tendency of 1,6-disubstituted cyclodecanes to undergo transannular cyclization. Bicyclo[4.4.1]undecan-1-ol (**13a**) is readily available by solvolytic cyclization of the *p*-toluenesulfonate of 6-methylenecyclodecanol (**9**) [14]. The tertiary hypochlorite **13b**, hypobromite **13c**, or hypoiodite **13d** are expected to break down to 6-(halomethyl)cyclodecanones (**11**, X = Cl, Br, or I) [18], however, the isomeric (4-halobutyl)cycloheptan-3-ones (**14b**, **14c**, and **14d**) were formed instead.

As before [11], the intramolecular *Wittig* reaction of the phosphonium bromide **11d** was performed in a high-boiling polyether such as tetra- or hexaethylene glycol dimethyl ether²) with the sodium or potassium salt of *t*-butyl alcohol, 2-methyl-2-butanol, triphenylmethanol, or 2-methylnonadecan-2-ol. An attempt to distil bicyclo[4.4.1]undec-1(11)-ene (**5**) from the reaction mixture and characterize it by spectroscopic methods and reactions at low temperature led to no compound with the expected properties of *Bredt* olefin **5**. Dimer **15** was isolated (10-35%) together with triphenylphosphine oxide and traces of benzene (*Scheme 2*). In some experiments, up to 1% of the isomeric bridgehead olefin bicyclo[4.4.1]undec-1-ene (**16**) was identified by comparison with authentic material prepared from alcohol **13a**.

If the *Wittig* reaction was conducted in the presence of 2,5-diphenylbenzo[*c*]-furan, the formation of the dimer **15** was suppressed and a 2:1 mixture of *endo* and *exo Diels-Alder* adducts **17** was isolated in 28% yield. Trapping with furan, however, was not effective.

Scheme 2



Structure elucidation of the dimer 15. - The hydrocarbon fraction from the *Wittig* reaction of **11d** contained *ca.* 95% of one dimer besides several minor products (GC.). Crystallization from ethanol gave a single compound, $C_{22}H_{36}$ (analysis, MS.).

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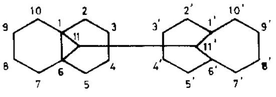
²) Tetraglyme and hexaglyme.

Surprisingly, the broad-band proton-decoupled ^{13}C-NMR. spectrum of this dimer displays 12 distinct lines between 20 and 48 ppm (relative to tetramethylsilane). This eliminates the symmetrical cyclobutane structures **18** and **19**, which would have been expected in analogy to previous experience with strained bridgehead olefins [19]. The possibility of an ene-dimer [20], *e.g.* **20**, was also dismissed, because such compounds would give 22 lines (except for accidental coincidences) and absorptions for vinylic carbon atoms.

Examination of the ^{1}H-NMR. spectrum reveals no signal for a vinylic proton, but the presence of a one-proton doublet ($J = 11.5$ Hz) at 0.98 ppm. This points to a proton on an otherwise fully substituted cyclopropane ring, joined to a tertiary carbon atom with a proton in exclusive or predominating *transoid* conformation [21], *i.e.* a structure unit **21**. A ^{13}C, ^{1}H coupling constant of 147 Hz is observed. This value is extremely low for a cyclopropane proton [22], but is reasonably explained by a change in hybridization at carbon as a consequence of steric compression [23].

The presence of the cyclopropyl group is confirmed in the IR. spectrum by a weak C–H absorption at 3010 cm^{-1} and additional bands at 1030 and 1040 cm^{-1} [24].



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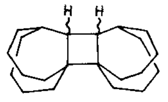

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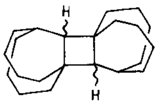

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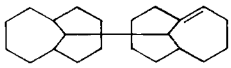

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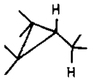

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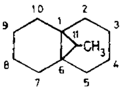

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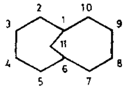

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The cyclopropane carbon bearing a proton (C(11)) is identified in the ^{13}C-NMR. at 35.9 ppm by its large residual coupling in different off-resonance proton-decoupled spectra. Together with one other tertiary carbon atom (C(11'), 41.3 ppm), it must lie in a symmetry plane (or axis) of the molecule. The only possible structure then obtained without extensive reorganization of the bicyclo[4.4.1]undecyl unit is shown in formula **15**.

Independent confirmation for structure **15** comes from a comparison with the ^{13}C-NMR. spectra of 11-methyltricyclo[4.4.1.0^{1,6}]undecane (**22**) [21]3) and bicyclo-[4.4.1]undecane (**23**) (see *Table*). The resonance for the quaternary cyclopropane carbon atoms C(1) and C(6) in **15** is observed at 22.1 ppm, close to the corresponding value in **22** (20.3 ppm). The two-carbon resonance at 40.4 ppm, a doublet in the off-resonance proton-decoupled spectrum, is assigned to the remaining tertiary bridgehead carbon atoms C(1') and C(6'). Excellent correlation is found between the chemical shift of the methylene carbon atoms in **15** and the corresponding carbon atoms in **22** and **23**: The only shift difference exceeding 1 ppm is observed at C(2')/C(5') and is readily accounted for by a shielding γ-effect of the substituent at C(11') present in **15** but missing in the model compound **23**.

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3) We thank Prof. *H. Günther* for the ^{13}C-NMR. spectrum of **22**.

Table. *^{13}C-NMR. spectra of dimer* **15** *and model compounds* **22**[3]) *and* **23**

	C(1)/C(6)	C(2)/C(5)	C(3)/C(4)	C(7)/C(10)	C(8)/C(9)	C(11)	
15	22.1	28.6	21.7[a])	34.3[b])	22.2[a])	35.9	
22	20.3	28.4	21.8[a])	34.2	22.1[a])	22.9	
23[d])							

	C(1')/C(6')	C(2')/C(5')	C(3')/C(4')	C(7')/C(10')	C(8')/C(9')	C(11')	CH_3
15	40.4	31.1	26.4[c])	33.9[b])	26.7[c])	41.3	
22							8.9
23[d])	36.5	34.3	27.0	34.3	27.0	37.0	

[a])[b])[c]) Assignment interchangeable on the same line.

[d]) For clarity, **23** is numbered like the corresponding part in **15**.

Discussion. - Bicyclo[4.4.1]undec-1(11)-ene (**5**), a tetramethylene-bridged *trans*-cycloheptene, could be generated by the intramolecular *Wittig* reaction, but was not isolated. This means that the *Bredt* olefin **5** is clearly less stable than methylene-bridged *trans*-cyclooctenes such as bicyclo[3.3.1]non-1-ene (**24**), bicyclo-[4.2.1]non-1(8)-ene (**25**), and bicyclo[4.2.1]non-1-ene (**26**) [11]. The synthetic approach to **5** even allows the conclusion that this olefin is less stable than the ethylene-bridged *trans*-cycloheptenes **1** and **2** [6], which survived harsher reaction conditions during their formation. This result is in contrast to *Köbrich*'s statement (rule A [1]) that, within a series of homologous bridgehead olefins, increasing the total number of carbon atoms should lead to less strained compounds. It is true that kinetic instability may not be related directly with strain energy, a thermodynamic property. However, from the discussion of the dimerization process *(vide infra)* it follows that the olefin **5** is kinetically even more stable than comparable *Bredt* olefins owing to steric interactions which inhibit dimerization in the usual mode.


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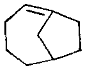
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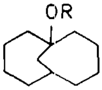

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That the *Bredt* olefin **5** is indeed formed, is confirmed by the trapping experiment with 2,5-diphenylbenzo[*c*]furan, by the structure of the dimer **15**, and by the isolation of an equivalent amount of triphenylphosphine oxide generated in the olefin-forming step of the *Wittig* reaction.

The formation of dimer **15** may be viewed as a concerted electrocyclic reaction or as a stepwise process *via* diradicals. The first intermediate might be the diradical **27**[4]), either as a *dl-* or a *meso*-form depending on whether two olefins with like or opposite chirality are combined. Bond formation at C(11) is favoured because this carbon atom is sterically less hindered than the bridgehead carbon atom C(1), and a tertiary radical is obtained instead of a secondary. Intramolecular hydrogen transfer from the opposite bridgehead C(6) *via* a five-membered transition state leads to a new diradical **28**, which readily collapses to the observed product **15**. For steric

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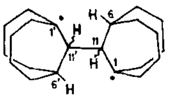
[4]) For general aspects of diradicals see [25].



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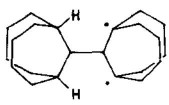

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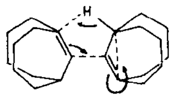

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reasons, formation of *meso*-**27** is probably preferred over *dl*-**27**, but both isomers lead to the same diradical **28**.

A concerted electrocyclic reaction may be depicted as in **29**. Such a bond reorganization corresponds to the ene-reaction, however, a cyclopropane ring is formed in place of a new double bond. Models suggest that twist and out-of-plane deformation of the strained double bond in **5** leads to a reasonable orbital overlap in **29** in a $[_{\pi}2_s + _{\pi}2_a + _{\sigma}2_a]$ reaction, if two molecules with opposite chirality are combined. At present there is no experimental evidence which would allow distinction between a diradical or a concerted process.

The question remains open as to why no cyclobutane dimers are found in analogy to prior experience with strained bridgehead olefins [19]. The head-to-head cyclobutane **18** (*cis* or *trans*) would be formed by collapse of the *cisoid* conformation of the diradical **27** (*meso* or *dl*, respectively). Models suggest that this reaction is highly unfavourable owing to nonbonding interactions of the ring methylene groups. Similar interactions exclude the formation of the ene-dimer **20** from the *cisoid* diradical **27** by hydrogen-transfer from C(2) to the opposite bridgehead radical center at C(1'), and the formation of head-to-tail cyclobutane dimers **19** from an analogous diradical bonded between C(11) and C(1'). A concerted $[_{\pi}2_a + _{\pi}2_s]$-cycloaddition or a concerted ene-reaction are inhibited for the same reason as the stepwise process. Because steric interactions of the tetramethylene bridges disfavour cyclobutane- or ene-dimer formation, the novel dimerization reaction to **15** becomes energetically feasible.

In some experiments, small amounts of the isomeric, unstrained bridgehead olefin bicyclo[4.4.1]undec-1-ene (**16**) were observed. This is formed by a formal 1,3-hydrogen-shift⁵). Products expected from an intermediate bridgehead carbenium ion, *e.g.* 1-bicyclo[4.4.1]undecyl ethers **30**, were not detected. A bridgehead radical is excluded as an intermediate, because no bicyclo[4.4.1]-undecane **23** is formed. However, the double bond isomerization is reasonably explained by way of an allylic anion formed in the strongly basic reaction medium.

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Experimental Part

General remarks. Melting points (m.p.) are corrected, boiling points (b.p.) are not corrected. IR. spectra were recorded on a *Perkin-Elmer* 125 or 177, and are given in cm^{-1}. The ^{1}H-NMR. spectra at 60 MHz were measured on a *Varian* EM 360, the ^{1}H-NMR. spectra at 90 MHz and the ^{13}C-NMR. spectra at 22.63 MHz on a *Bruker* WH-90 *Fourier* transform spectrometer by Mr. *K. Aegerter.* The chemical shift values are in ppm relative to tetramethylsilane (TMS) as internal standard ($\delta = 0$), and

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5) For other examples of formal 1,3-hydrogen-shifts in strained bridgehead olefins see [26].

the coupling constants J in Hz. The multiplicity is abbreviated as follows: s=singlet, d=doublet, t=triplet, qa=quartet, m=multiplet. Gas chromatography (GC.) analyses and separations were carried out on a *Perkin-Elmer* 3920. Mass spectra were recorded by Mr. *A. Raas* on a *AEI*-MS 30 at 70 eV. Elemental analyses were carried out by Mr. *E. Thommen.*

Usual work-up means extraction (3 times) with the specified solvent followed by washing the extracts with water and brine, drying ($MgSO_4$), and evaporation *in vacuo* (i.V.).

6-Methylidenecyclodecanol (**9**) was prepared from 6-hydroxycyclodecanone (**8**) [13] and methylenetriphenylphosphorane in dimethylsulfoxide according to [14] in 78% yield, m.p. 41-42°. - IR. (CCl_4): 3630, 3070, 2920, 2860, 1635 (C=C), 1445, 1000, 880. - ^{1}H-NMR. (CCl_4): 0.8-2.8 (m, 17 H); 3.8 (br. s, 1 H, OH); 4.8 (s, 2 H, $=CH_2$).

$C_{11}H_{20}O$ (168.28) Calc. C 78.51 H 11.98% Found C 78.68 H 12.12%

6-(Hydroxymethyl)cyclodecanol (**10**). A solution of 0.84 g (5.0 mmol) **9** in dry THF (2 ml) was treated with 4.2 ml of a 1.2M solution of diborane in THF at 0° under N_2. After 20 h at 25°, the solution was stirred with 1 ml 3N NaOH and 0.8 ml 30% H_2O_2-solution at 40-50° for 1 h. Usual work-up with ether and distillation in a bulb tube at 135-150°/0.01 Torr gave 0.87 g (93%) of the diol **10** as a viscous, colourless oil. An analytically pure sample was obtained by column chromatography on silica gel with ether/methanol, yield: 81%. - IR. (CH_2Cl_2): 3605 (OH), 2930, 2865, 1480, 1440, 1110, 1040. - ^{1}H-NMR. ($CDCl_3$): 0.6-2.2 (m, 17 H); 2.5 (s, 2 H, OH); 3.4 (d, J=6, 2 H, CH_2OH); 3.8 (m, 1 H, $CHOH$).

$C_{11}H_{22}O_2$ (186.30) Calc. C 70.92 H 11.90% Found C 70.81 H 12.06%

6-(Hydroxymethyl)cyclodecanone (**11a**). Following *Caubère et al.* [15], 4.5 ml of a 2M solution of Br_2 in CH_2Cl_2 were added dropwise to a well-stirred mixture of 1.64 g (8.8 mmol) **10**, 0.32 g (1.8 mmol) hexamethylphosphoric triamide, 8% aqueous $NaHCO_3$-solution (33 ml), and CH_2Cl_2 (30 ml) at 0°. After 5 min at 20°, the heterogeneous mixture was diluted with CH_2Cl_2 and worked up as usual. Column chromatography on silica gel in petroleum ether/ether 2:1 gave 1.54 g (95%) of the hydroxyketone **11a** as a colourless oil. - IR. (CCl_4): 3650, 2935, 2870, 1705 (C=O), 1460, 1445, 1035. - ^{1}H-NMR. (CCl_4): 0.5-2.7 (m, 17 H); 2.8 (s, 1 H, OH); 3.3 (d, J=4.5, 2 H, CH_2OH).

$C_{11}H_{20}O_2$ (184.28) Calc. C 71.69 H 10.94% Found C 71.42 H 11.20%

6-(Bromomethyl)cyclodecanone (**11c**). To a stirred solution of 10.9 g (59 mmol) **11a** and 9.9 ml (71 mmol) triethylamine in CH_2Cl_2 (100 ml), 5.0 ml (65 mmol) freshly distilled methanesulfonyl chloride were added dropwise at −10°. After 30 min at that temperature, the reaction mixture was diluted with cold CH_2Cl_2, washed with ice-water and cold brine, dried ($MgSO_4$), and evaporated i.V. at 0°. Attempts to purify the crude 6-(methanesulfonyloxymethyl)cyclodecanone (**11b**, 15.5 g, 100%) were all fruitless. - IR. (CCl_4): 2930, 2860, 1700, 1365, 1340, 1175 (OSO_2), 945. - ^{1}H-NMR. (CCl_4): 0.5-2.8 (m, 17 H); 2.9 (s, 3 H, CH_3SO_2); 3.9 (d, J=6, 2 H, CH_2OSO_2).

Crude mesylate **11b** (59 mmol) and 10.3 g (118 mmol) LiBr were refluxed in dry acetone (60 ml) for 4 h. The solution was concentrated *in vacuo* and worked up with ether as usual. Crystallization from ether and cyclohexane gave 11.7 g (80%) of 6-(bromomethyl)cyclodecanone (**11c**) as white needles, m.p. 64.5-65°. - IR. (CCl_4): 2930, 2860, 1700, 1440, 635. - ^{1}H-NMR. (CCl_4): 0.5-2.1 (m, 13 H); 2.2-2.8 (m, 4 H); 3.2 (d, J=4.5, 2 H, CH_2Br).

$C_{11}H_{19}BrO$ (247.19) Calc. C 53.44 H 7.74 Br 32.33% Found C 53.49 H 7.84 Br 32.23%

[(6-Oxocyclodecyl)methyl]triphenylphosphonium bromide (**11d**). A mixture of 0.99 g (4.00 mmol) **11c** and 1.05 g (4.00 mmol) triphenylphosphine in dry ether (4 ml) was sealed in a Pyrex pressure tube and heated to 130° for 85 h. The solid product was washed with several portions of dry ether, dissolved in CH_2Cl_2, evaporated, and dried over P_2O_5 for 48 h at 0.01 Torr, which gave 1.77 g (87%) of the phosphonium bromide **11d** as an extremely hygroscopic, glass-like solid, which was not purified further. - IR. ($CHCl_3$): 2930, 1690, 1435, 1110, 995. - ^{1}H-NMR. ($CDCl_3$): 0.7-2.0 (m, 13 H); 2.1-3.0 (m, 4 H); 3.2-3.8 (m, 2 H, CH_2P); 7.2-8.2 (m, 15 H, ArH).

6-Methylidenecyclodecanone (**12**). A solution of 0.84 g (5.0 mmol) 6-methylenecyclodecanol (**11a**) in dry pyridine (3 ml) was added dropwise to a suspension of the complex prepared with 1.45 g (14.5 mmol) CrO_3 and pyridine (10 ml) [16]. The reaction mixture was stirred for 20 h at 25°, then filtered with suction. The filtrate was diluted with water (50 ml), then worked up with benzene/ether

1:1 as usual. Distillation in a bulb tube at 45-60°/0.02 Torr gave 0.84 g (100%) ketone **12** as a waxy solid, which was recrystallized (3×) from petroleum ether giving 0.69 g (83%) of white crystals, m.p. 31-32°. - IR. (CCl_4): 3070, 2920, 2880, 1700 (C=O), 1635 (C=C), 1435, 880. - ^{1}H-NMR. (CCl_4): 0.8-2.8 (*m*, 16 H); 4.8 (*s*, 2 H, =CH_2).

$C_{11}H_{18}O$ (166.26) Calc. C 79.46 H 10.92% Found C 79.35 H 11.18%

Attempted addition of HBr to 6-methylenecyclodecanone (**12**). Ketone **12** in pentane was placed in a quartz photochemical reaction vessel, flushed with N_2, and cooled to 25°, 0°, or −40°. Dry HBr was bubbled through the solution while it was irradiated with a low-pressure Hg-lamp for 2 to 10 min. Excess HBr was blown out with N_2, and the remaining solution washed with aqueous $Na_2S_2O_3$-solution, dried, and evaporated. The crude product consisted in all cases of 3 to 5 main components (GC.), none of which proved to be 6-(bromomethyl)cyclodecanone **11c**. A similar product composition was obtained in a reaction without irradiation.

Bicyclo[4.4.1]undecan-1-ol (**13a**) was isolated from the solvolysis mixture of 6-methylidenecyclodecyl *p*-toluenesulfonate in aqueous acetone [14]. From a column of silica gel, petroleum ether/ether 1:1 eluted first a complex hydrocarbon fraction (40%), then bicyclo[4.4.1]undecan-1-ol (**13a**) (55%), m.p. 56-57° (from ether at −20°, [14]: 55-56°). - IR. (CCl_4): 3600 (OH), 2910, 2850, 1460, 1445, 1040, 1000, 980, 910. - ^{1}H-NMR. (CCl_4): 1.2-1.8 (*m*, 16 H, including OH); 1.8-2.1 (*m*, 4 H).

$C_{11}H_{20}O$ (168.28) Calc. C 78.51 H 11.98% Found C 78.31 H 11.81%

Bicyclo[4.4.1]undec-1-ene (**16**) was separated from above hydrocarbon mixture by preparative GC. (SE-30, 150°). It was also obtained from alcohol **13a** with $POCl_3$ in pyridine [27] (84%). - IR. (film): 3040*w* (=CH), 2910, 2850, 1660*w*, 1445, 845. - ^{1}H-NMR. ($CDCl_3$): 1.2-2.8 (*m*, 17 H); 5.4 (*t*, *J*=6.5, 1 H, =CH). - ^{13}C-NMR. ($CDCl_3$): 142.2 (*s*, C(1)); 123.8 (*d*, C(2)); 38.4, 36.1, 35.8, 32.3 and 31.0 (each *t*, CH_2); 30.5 (*d*, C(6)); 27.0; 24.6; 21.3 (each *t*, CH_2).

$C_{11}H_{18}$ (150.27) Calc. C 87.92 H 12.08% Found C 88.01 H 12.30%

Hydrogenation of olefin **16** over 10% Pd/C in methanol led to *bicyclo[4.4.1]undecane* (**23**) [28]. - ^{13}C-NMR. ($CDCl_3$): 37.0 (*s*, C(11)); 36.5 (*d*, C(1), C(6)); 34.3 (*t*, C(2), C(5), C(7), C(10)); 27.0 (*t*, C(3), C(4), C(8), C(9)).

Synthesis and decomposition of 1-bicyclo[4.4.1]undecyl hypobromite (**13c**). A solution of 0.91 g (5.7 mmol) Br_2 in CCl_4 (5 ml) was added dropwise with stirring to 385 mg (2.29 mmol) bicyclo[4.4.1]undecan-1-ol (**13a**) and 1.47 g (6.79 mmol) mercuric oxide in CCl_4 (15 ml) at 4° under N_2 in the dark. After 30 min, the reaction mixture was refluxed for 2 h under ordinary laboratory light. The cooled suspension was filtered and worked up as usual. Chromatography of the crude product over silica gel with petroleum ether/ether and distillation in a bulb tube at 105°/0.2 Torr gave 79 mg (14%) of *(4-bromobutyl)cycloheptan-3-one* **14c**. - IR. (CCl_4): 2930, 2860, 1705 (C=O), 1445, 1240, 1120. - NMR. (CCl_4): 3.35 (*t*, *J*=6, 2 H, CH_2Br); 2.35 (*m*, 4 H, CH_2CO); 1.1-2.2 (*m*, 13 H).

$C_{11}H_{19}BrO$ (247.19) Calc. C 53.44 H 7.74 Br 32.33% Found C 53.44 H 7.90 Br 32.52%

The expected 6-(bromomethyl)cyclodecanone **11c** was formed in less than 0.5% yield (GC.).

The corresponding reaction of alcohol **13a** with lead tetraacetate and I_2 in refluxing benzene gave *(4-iodobutyl)cycloheptan-3-one* **14d** in 25% yield after chromatography. - IR. (CCl_4): 2930, 2860, 1700 (C=O), 1445. - NMR. (CCl_4): 3.15 (*t*, *J*=6, 2 H, CH_2I); 2.35 (*m*, 4 H, CH_2CO); 1.1-2.1 (*m*, 13 H).

Hypochlorite **13c** was formed from the alcohol **13a**, aqueous sodium hypochlorite and acetic acid in CCl_4. Thermal or photolytic decomposition of **13c** gave a low yield (13% or 6%, respectively) of *(4-chlorobutyl)cycloheptan-3-one* **14b**. - IR. (CCl_4): 2930, 2860, 1700 (C=O), 1445. - NMR. (CCl_4): 3.45 (*t*, *J*=6, 2 H, CH_2Cl); 1.1-2.5 (*m*, 17 H).

Intramolecular Wittig *reaction of [(6-oxocyclodecyl)methyl]triphenylphosphonium bromide* (**11d**). *Dimer* **15**. A flask containing a suspension of 1.56 g (3.1 mmol) **11d** and 0.38 g (3.4 mmol) potassium *t*-butoxide in dry hexaglyme (9 ml, prepared from the dichloride of tetraethylene glycol and sodium 2-methoxyethoxide [29]) was connected to a cold trap (−78°), evacuated to 0.2 Torr, and gradually heated to 140° with stirring over a period of 4 h. The content of the cold trap was dissolved in cold (−70°) CS_2 and transferred to a NMR. tube, rigorously excluding moisture and O_2. The ^{1}H-NMR. spectrum at −63° showed *t*-butyl alcohol, benzene, the vinyl proton of the isomeric olefin **16**, and some aliphatic material. A 2% yield of the expected olefin **5** would have been detected. GC. analysis of this solution showed olefin **16** (1% yield), dimer **15** (4% yield), but neither bicyclo[4.4.1]undecane **23** nor any compound with the expected retention time of 1-*t*-butoxybicyclo[4.4.1]undecane **30**.

The reaction mixture was worked up with pentane as usual. Column chromatography on silica gel in cyclohexane separated a hydrocarbon fraction from triphenylphosphine oxide (0.20 g, 23%), hexaglyme, and more polar material. The hydrocarbon fraction contained 95% of one dimer besides several minor products (GC., SE-54, 20 m capillary column). Crystallization from ethanol gave 92 mg (20%) of 11-(11'-bicyclo[4.4.1]undecyl)tricyclo[4.4.1.$0^{1,6}$]undecane (**15**), m.p. 132-133°. - IR. (CCl_4): 3010*w*, 2930, 2860, 1455, 1040, 1030. - ^{1}H-NMR. (90 MHz, $CDCl_3$): 1.2-2.0 (*m*, 35 H); 0.98 (*d*, $J_{H,H}$ = 11.5, $J_{C,H}$ = 147, 1 H, H-C(11)). - ^{13}C-NMR. ($CDCl_3$): 41.3 (*d*, C(11')); 40.4 (*d*, C(1') and C(6')); 35.9 (*d*, C(11)); 34.3, 33.9, 31.1, 28.6, 26.7, 26.4 and 22.2 (each *t*, CH_2); 22.1 (*s*, C(1), C(6)); 21.7 (*t*, CH_2). - MS.: 301 (3), 300 (M^+, 12), 149 (43), 136 (100), 121 (20), 107 (20), 95 (39), 81 (35), 67 (39).

$C_{22}H_{36}$ (300.54) Calc. C 87.92 H 12.08% Found C 87.69 H 12.24%

Other conditions for the generation of **15**. Sodium hydride and 2-methyl-2-butanol in tetraglyme at 120°/12 Torr [11]: 36% **15**. Potassium hydride and triphenylmethanol in hexaglyme at 140°/0.1 Torr: 25% **15**. Hexaglyme was cleaved to vinyl ethers by excess potassium hydride. Potassium 2-methyl-2-nonadecanoate (prepared from the alcohol [30] and potassium hydride in dimethoxyethane), with or without dicyclohexyl-18-crown-6 in hexaglyme at 140°/0.1 Torr: 20% and 18% **15**, respectively. No olefin **16** was formed in the presence of crown ether.

Adduct of **5** *with 2,5-diphenylbenzo*[c]*furan*. To a suspension of 0.70 g (1.4 mmol) phosphonium bromide **11d**, 3.0 mmol sodium hydride (washed oil-free with pentane), and 0.19 g (0.70 mmol) of 2,5-diphenylbenzo[*c*]furan in dry tetraglyme (4 ml) under N_2, 0.13 g (1.5 mmol) of 2-methyl-2-butanol were added dropwise. The mixture was heated at 140° for 4 h with stirring. Usual work-up with benzene and filtration through a short column of silica gel gave a crude product (0.22 g) which contained considerable amounts of unreacted 2,5-diphenylbenzo[*c*]furan. It was dissolved in benzene (3 ml), stirred with 0.080 g (0.80 mmol) of maleic anhydride for 4 h at 25°, evaporated i.V., then refluxed in ethanol/4N NaOH 3:1 for 3 h and worked up with benzene. The crude adduct **17** (0.165 g, 28%) was separated into *endo* and *exo* isomers (2:1) by TLC. on silica gel plates with CCl_4.

Endo-**17**, m.p. 222-223° (from 95% ethanol). - IR. (CCl_4): 3065, 3030, 2920, 2860, 1605, 1500, 1460, 1445, 1280, 1000, 980, 700, 675, 660. - ^{1}H-NMR. (90 MHz, $CDCl_3$): 0.8-1.9 (*m*, 16 H); 2.5 (br. *m*, 1 H); 2.78 (*d*, *J* = 4.7, *exo*-H[31]); 7.0-7.8 (*m*, 14 H, ArH). - MS.: 420 (M^+, 0.2), 283 (30), 270 (100), 241 (9), 239 (5).

$C_{31}H_{32}O$ (420.60) Calc. C 88.53 H 7.67% Found C 88.32 H 7.56%

Exo-**17**, m.p. 211-212° (from 95% ethanol). - IR. (CCl_4): 3065, 3030, 2920, 2860, 1600, 1490, 1445, 1295, 990, 700, 675, 660. - ^{1}H-NMR. (90 MHz, $CDCl_3$): 0.7-2.0 (*m*, 16 H); 2.4 (br. *m*, 1 H); 2.60 (*d*, *J* = 5.2, *endo*-H[31]); 7.0-7.8 (*m*, 14 H, ArH). - MS.: 420 (M^+, 0.2), 283 (9), 270 (100), 241 (12), 239 (7).

$C_{31}H_{32}O$ (420.60) Calc. C 88.53 H 7.67% Found C 88.40 H 7.64%

Attempted trapping of **5** *with furan*. A suspension of phosphonium bromide **11d** and an equivalent amount of potassium *t*-butoxide in tetraglyme/furan 1:5 was refluxed for 96 h or heated in a sealed pressure Pyrex tube at 120-130° for 4 h. Work-up gave **15** (13% and 39% respectively) and a trace of olefin **16** (0.2%), but no compound with the expected properties of a *Diels-Alder*-adduct of *Bredt* olefin **5** with furan.

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